2-HYDROXYACETYT-FURAN FROM SUCROSE

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By

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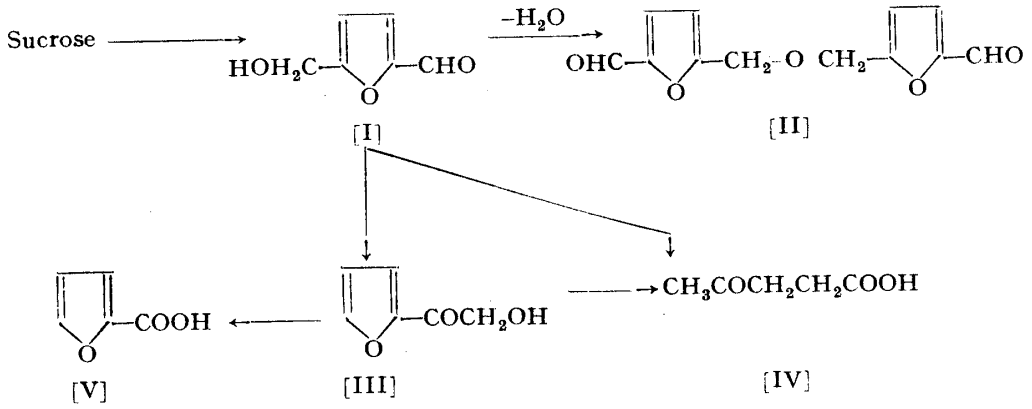
(*Received August 31, 1954*)

For many years, it has been studied that the dehydrolytic degradation of hexoses, or polysaccharides in neutral or acidic aqueous solution yielded furan derivatives. 5-Hydroxymethyl-furfural [I] was discovered by Düll (1) when investigating the action of aqueous oxalic acid on polysaccharides. Kiermayer *et al.* (2) also obtained it by similar treatment of sucrose, and observed that under the conditions employed, the glucose portion of sucrose molecule was largely recoverable. Haworth and Jones (3) re-examined the preparation of I from sucrose, and isolated the crude aldehyde in 54% yield based on the fructose portion of sugar molecule. Following removal of I, the residue was oxidized by the action of nitric acid, and saccharic acid was isolated in a yield almost identical to that similar oxidation of glucose. Thus, it was early recognized that ketohexoses are more readily transformed into I than aldohexoses. In 1934, Aso (4) obtained I and its ether [II] [oxybis–(5-methylene-furfural)] as the autoclaved products of agar-agar, starch, sucrose and fructose, and also he prepared these from sucrose by a method similar to that described by Feulgen and Imhäuser (5). On the II's formation mechanism, Aso proposed that II was formed by the dehydrolytic condensation of initially formed I.

Recently, Miller *et al* (6) reported on the isolation of another furan compound, 2-hydroxyacetyl-furan (2-furoylcarbinol) [III], from the acid catalyzed dehydration of sucrose in aqueous solution.

The present investigation was undertaken to research the quesions whether III may be formed from I or may be an intramoleuclar rearrangement of I, moreover that it may be related to the formation of levulinic acid [IV]. We here report our findings that I, II and III were obtained by the acid catalyzed dehydration of sucrose as that described by Miller, moreover that III was formed from I without oxalic acid as a catalyser, and also IV and furoic acid [V] resulted from III by similar treatment using dilute hydrochloric acid as an acid catalyser, but II was unchanged to III.



Experimental

(1) *2-Hydroxyacetyl-furan [III] from sucrose*

Sucrose 240 g, oxalic acid 2.4 g (1% oxalic acid by weight of sucrose) and water 800 ml were heated in an autoclave at 140°C for 3 hrs. After cooling, the reaction mixture was filtered with suction through a Büchner funnel, to remove a humus produced, and neutralized with lime, then extracted three times with ethyl acetate. After removal of the solvent, the residue was distilled under reduced pressure. In the course of the distillation, at 130°C/15 mm Hg, we observed the appearance of a crystalline material which sublimed on the walls of the water-cooled condenser. When this crystalline material was recrystallized from n-hexane, it was a colorless needle, m.p. 83~85°C, yield 0.2 g. The melting point of this substance was not depressed by admixture with the authentic 2-hydroxyacetly-furan which was prepared by the hydrolysis of 2-diazoacetyl-furan (7).

Microanaylsis	Found	C % 57.27	H % 5.00
	Calcd. for $C_6H_6O_3$	C % 57.14	H % 4.80

Its benzoate melted at 74~76°C.

Then 8.5 g of 5-hydroxymethyl-furfural was obtained by distlling at 145~150°C/15 mm Hg. The residue of the distillation was extracted with ethanol, and 5-hydroxymethyl-furfural-ether [oxybis-(5-methylene-furfural)] was obtained. When it was recrystallized from ethanol by the aid of charcoal, it was a white plate, m.p. 112°C.

(2) *2-Hydroxyacetyl-furan [III] from 5-hydroxymethyl-furfural [I]*

5-Hydroxymethyl-furfural 10 g, oxalic acid 0.3 g and water 100 ml were heated in an autoclave at 140°C for 3 hrs. According to the treating described above, 2-hydroxyacetyl-furan 0.2 g and 5-hydroxymethyl-furfural-ether 0.2 g were obtained, and then 2 g of the starting material was recovered.

(3) *2-Hydroxyacetyl-furan [III] from 5-hydroxymethyl-furfural [I] without an acid catalyser*

Without an acid catalyser, 5-hydroxymethyl-furfural 4 g and water 40 ml were heated in an autoclave at 140°C for 3 hrs. The procedures were essentially the same as those described above, and 0.05 g of 2-hydroxyacetyl–furan was obtained. When the distilled residue was extracted with benzene, a mixture of 5-hydroxymethyl-furfural-ether and 2-hydroxyacetyl-furan was obtained, and then from the mixture, a small amount of the latter was isolated by sublimation under reduced pressure.

(4) *The heating of 5-hydroxymethyl-furfural-ether [II] in acidic solution*

5-Hydroxymethyl-furfural-ether 2 g, oxalic acid 0.06 g and water 20 ml were treated as in the foregoing experiment. The starting material was unchanged and recovered with the original amount.

(5) *Levulinic acid [IV] from sucrose* (8)

Sucrose 100 g, 300 ml of 1.5 % hydrochloric acid were heated in an autoclave at 165~170°C for 1 hr. After cooling, the reaction mixture was filtered, then extracted with ether. The ether extract was shaked with 10 % Na_2CO_3 to remove of levulinic acid produced, and the solution of Na_2CO_3 was acidified, then re-extracted with ether. 30 g of levulinic acid was obtained from the ether extract. The portions which were not removed by the solution of Na_2CO_3 seemed to be 5-hydroxymethyl-furfural, its ether and 2-hydroxyacetyl-furan, but these were not obtained.

(6) *Dehydration of sucrose by 0.3% hydrochloric acid*

When sucrose 100 g, 300 ml of 0.3 % hydrochloric acid were treated as shown above, 2 g of levulinic acid was obtained, but the other furan derivatives presumed were not obtained.

(7) *Levulinic acid [IV] and furoic acid [V] from 2-hydroxyacetyl-furan [III]*

2-Hydroxyacetyl-furan 0.5 g and 1.5 % hydrochloric acid 30 ml were heated in an autoclave at 170°C for 1 hr. The procedures were essentially the same as those described above. It was recognized by the application of paper partition chromatography that levulinic and furoic acid were the result from 2-hydroxyacetyl-furan by the action of hydrochloric acid. The main portion of this product was a colorless crystal melting at 125~130°C, yield 0.4 g. The mixture of obtained crystal and the authentic furoic acid gave no deprssion of melting point.

Summary

(1) By the acid catalyzed dehydration of sucrose, 5-hydroxymethyl-furfural, 5-hydroxymethyl-furfural-ether and 2-hydroxyacetyl-furan were obtained.

(2) 2-Hydroxyacetyl-furan was formed from 5-hydroxymethyl-furfural, and also without an acid catalyser.

(3) By using dilute hydrochloric acid as an acid catalyser, levulinic acid

only was obtained from sucrose, the other was not obtained.

(4) By similarly heating 2-hydroxyacetyl-furan and dilute hydrochloric acid, it was recognized that 2-hydroxyacetyl-furan resulted levulinic and furoic acid.

An attempt to explain the formation mechanism of 2-hydroxyacetyl-furan was unsuccessful, but the study of the formation of this compound is now in progress.

Acknowledgement : We experss our deep gratitude to Mr. kazuo Kobayashi for his cooperation and the microanalyzer of the Department of Agricultural Chemistry, Faculty of Agrciulture, Tokyo University.

This work was presented at the local meeting of the Agricultural Chemical Society of Japan, Sendai, June 15, 1954.

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